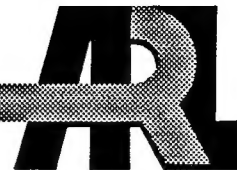


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# The Theoretical Calculation of Vibrational Circular Dichroism Spectra

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## 1. INTRODUCTION

We report a major advance in the *ab initio* theoretical prediction of vibrational circular dichroism (VCD) spectra. This advance permits useful predictions of VCD spectra for much larger molecules than heretofore accessible. As a result, the practical utility of VCD spectroscopy in studying the stereochemistry of chiral molecules is greatly enhanced.

Specifically, we report the first *ab initio* calculations of VCD spectra based on harmonic force fields obtained using density functional theory (DFT). DFT is increasingly used in the calculation of molecular properties (Ziegler 1991; Labanowski and Andzelm 1991). Its growing popularity is due to (1) the development of new and more accurate density functionals; (2) the increasing versatility, efficiency, and availability of DFT codes; and (3) the superior ratio of accuracy to effort exhibited by DFT computations relative to other *ab initio* methodologies. It has been clear for some time that harmonic force fields calculated via DFT are substantially more accurate than self-consistent field (SCF) force fields, and are comparable in accuracy to force fields calculated using Moller-Plesset second order perturbation theory (MP2) (Ziegler 1991; Labanowski and Andzelm 1991; Andzelm and Wimmer 1992; Johnson, Gill, and Pople 1993; Handy, Murray, and Amos 1993). Very recently there have been two very important developments that greatly enhance the utility of DFT in predictions of vibrational spectra. First, a new class of density functionals has been introduced—the so-called hybrid functionals—which are significantly more accurate than prior functionals (Becke 1993). Second, efficient analytical derivative techniques have been implemented for the calculation of second derivatives of the energy with respect to nuclear displacement (Johnson and Frisch 1993, 1994). As a results of these developments, it is now possible to calculate harmonic force fields of an accuracy comparable to that of MP2 force fields with substantially less computational effort. In this report, we document the practicability and illustrate the accuracy of calculations of VCD spectra based on DFT force fields calculated using a hybrid density functional. The molecules, 4-methyl-2-oxetanone, 1, 6,8-dioxabicyclo[3.2.1] octane, 2, and 1,7,7-trimethylbicyclo[2.2.1] heptan-2-one (camphor)k, 3, are shown in Figure 1.

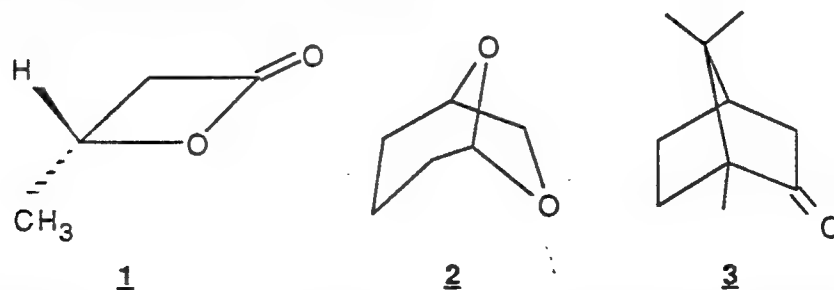


Figure 1. Molecules studied in this work: 1, 4-methyl-2-oxetanone; 2, 6,8-dioxabicyclo[3.2.1] octane; 3, and 1,7,7-trimethylbicyclo[2.2.1] heptan-2-one.

Why is the advance we report so important for VCD spectroscopy? Since the discovery of VCD in the 1970s (Holzwarth et al. 1974; Nafie, Cheng, and Stephens 1975; Nafie, Keiderling, and Stephens 1976; Stephens and Clark 1979), the primary justification for continued study of VCD has been its potential utility in the elucidation of the stereochemistry of chiral molecules, both natural and synthetic. However, to date, VCD spectroscopy has made very little impact. While the measurement of VCD spectra has become almost routine (Nafie 1988; Keiderling 1990), the extraction of structural information from spectra has not. The latter requires a methodology for accurately predicting VCD spectra. This, in turn, requires *ab initio* computational methods. While much progress has been made since the earliest *ab initio* calculations of VCD spectra (Lowe, Stephens, and Segal 1986; Jalkanen et al. 1987, 1988; Kawiecki et al. 1988), the calculation of accurate harmonic force fields has remained problematical. It was clear a long time ago that SCF force fields are insufficiently accurate to provide useful predictions of VCD spectra (except in the case of a few, very small symmetrical molecules). MP2 force fields provide much more accurate spectra (Amos, Handy, and Palmieri 1990; Stephens et al. 1993; Stephens et al. 1994). However, the computational demands of MP2 force fields increase very rapidly with increasing molecular size, and useful calculations on such molecules as camphor (Devlin and Stephens 1994) have only been practicable on very large supercomputers. As we demonstrate here, DFT provides a way out of this dilemma. It includes correlation but without the extra cost of MP2 calculations. As a result, the way is now clear to the routine calculation of VCD spectra with useful accuracy on a wide range of molecules up to a very considerable size. Widespread application of VCD spectroscopy is now, finally, close at hand.

## 2. METHODS

Dipole and rotational strengths,  $D_i$  and  $R_i$ , of a fundamental transition in the  $i$ th normal mode of energy  $\hbar\omega_i$  are calculated within the harmonic approximation using the equations (Stephens 1985, 1987, 1989):

$$D_i = \left| \langle 0 \left| \bar{\mu}_{el} \right| 1 \rangle_i \right|^2$$

$$R_i = \text{Im} \left[ \langle 0 \left| \bar{\mu}_{el} \right| 1 \rangle_i \cdot \langle 1 \left| \bar{\mu}_{mag} \right| 0 \rangle_i \right] \quad (1)$$

where the electric and magnetic transition moments are given by

$$\begin{aligned} \langle 0 | (\mu_{el})_\beta | 1 \rangle_i &= \left( \frac{\hbar}{2\omega_i} \right)^{1/2} \sum_{\lambda, \alpha} P_{\alpha\beta}^\lambda S_{\lambda\alpha, i} \\ \langle 0 | (\mu_{mag})_\beta | 1 \rangle_i &= - \left( 2\hbar^3 \omega_i \right)^{1/2} \sum_{\lambda, \alpha} M_{\alpha\beta}^\lambda S_{\lambda\alpha, i}. \end{aligned} \quad (2)$$

Normal coordinates  $Q_i$  are given by

$$X_{\lambda\alpha} = \sum_i S_{\lambda\alpha, i} Q_i \quad (3)$$

where  $X_{\lambda\alpha}$  are Cartesian displacement coordinates. Atomic polar tensors (APTs) are given by

$$P_{\alpha\beta}^\lambda = \left[ \frac{\delta}{\delta X_{\lambda\alpha}} \langle \Psi_G | (\mu_{el})_\beta | \Psi_G \rangle \right]. \quad (4)$$

where  $\Psi_G$  is the ground electronic state wavefunction. Atomic axial tensors (AATs) are given in the distributed origin (DO) gauge (Stephens 1987; Jalkanen et al. 1988; Stephens et al. 1989, 1990) and with respect to molecular origin O by

$$\left( M_{\alpha\beta}^\lambda \right)^* = \left( I_{\alpha\beta}^\lambda \right) \bar{R}_\lambda^* + \frac{i}{4\hbar c} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{\lambda\gamma}^* P_{\alpha\delta}^\lambda \quad (5)$$

where  $I_{\alpha\beta}^\lambda$  is given by

$$I_{\alpha\beta}^\lambda = \left\langle \left( \frac{\delta \Psi_G}{\delta X_{\lambda\alpha}} \right) \middle| \left( \frac{\delta \Psi_G}{\delta H_\beta} \right) \right\rangle \quad (6)$$

and  $(I_{\alpha\beta}^{\lambda})^{\bar{R}_{\pi}^{\circ}}$  is calculated with the origin at the equilibrium position of nucleus  $\pi$ ,  $\bar{R}_{\pi}^{\circ}$ . The "local" AATs,  $(I_{\alpha\beta}^{\lambda})^{\bar{R}_{\pi}^{\circ}}$ , are, in turn, obtained via the identity

$$(I_{\alpha\beta}^{\lambda})^{\bar{R}_{\pi}^{\circ}} = (I_{\alpha\beta}^{\lambda})^{\circ} - \frac{i}{4\hbar c} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{\lambda\gamma}^{\circ} E_{\alpha\delta}^{\lambda}(\pi) \quad (7)$$

where  $E_{\alpha\beta}^{\lambda}(\pi)$  is the electronic component of the APT in the momentum representation (Stephens et al. 1990; Amos, Jalkanen, and Stephens 1988). The DO gauge provides origin-independent rotational strengths.

For the present work, DFT Cartesian harmonic force fields have been calculated for 1–3 using analytical derivative techniques via the program GAUSSIAN 92/DFT (Frisch et al. 1992, 1993). APTs are calculated simultaneously. Three density functionals have been employed: LSDA, BLYP, and the hybrid functional Becke3LYP (henceforth B3LYP). The LSDA functional (also referred to elsewhere as SVWN) uses the standard local exchange functional (Becke 1989) and the local correlation functional of Vosko, Wilk, and Nusair (1980). The BLYP functional combines the standard local exchange functional with the gradient correction of Becke (1989) and uses the Lee-Yang-Parr (1988) correlation functional (which also includes density gradient terms). The B3LYP functional is a hybrid of exact (Hartree-Fock) exchange with local and gradient-corrected exchange and correlation terms, as first suggested by Becke (1993a). The exchange-correlation functional proposed and tested by Becke (1993b) was

$$E_{xc} = (1 - a_0) E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} + E_c^{LSDA} + a_c \Delta E_c^{PW91}. \quad (8)$$

Here  $\Delta E_x^{B88}$  is Becke's gradient correction to the exchange functional and  $\Delta E_c^{PW91}$  is the Perdew-Wang gradient correction to the correlation functional (Perdew 1991). Becke (1993b) suggested coefficients  $a_0 = 0.2$ ,  $a_x = 0.72$  and  $a_c = 0.81$  based on fitting to heats of formation of small molecules. Only single-point energies were involved in the fit; no molecular geometries or frequencies were used. The B3LYP functional in GAUSSIAN 92/DFT uses the values of  $a_0$ ,  $a_x$ , and  $a_c$  suggested by Becke, but uses LYP for the correlation functional. Since LYP does not have an easily separable local component, the VWN local correlation expression has been used to provide the different coefficients of local and gradient corrected correlation functionals:

$$E_{xc}^{B3LYP} = (1 - a_o) E_x^{LSDA} + a_o E_x^{HF} + a_x \Delta E_x^{B88} + a_c E_c^{LYP} + (1 - a_c) E_c^{VWN}. \quad (9)$$

The standard fine grid in GAUSSIAN 92/DFT (Trucks and Frisch, to be published) was used in all DFT calculations. This grid was produced from a basic grid having 75 radial shells and 302 angular points per radial shell for each atom, and reducing the number of angular points for different ranges of radial shells, leaving about 7,000 points per atom while retaining similar accuracy to the original (75,302) grid. Becke's (1988) numerical integration techniques were employed. In addition, in the case of 1, Cartesian harmonic force fields and APTs were also calculated at the SCF and MP2 levels of approximation using analytical derivative techniques via GAUSSIAN 92 (Frisch et al. 1992, 1993). Local AATs were calculated for 1-3 at the SCF level of approximation using analytical derivative techniques (Amos, Jalkanen, and Stephens 1988; Amos et al. 1987) via CADPAC (Amos 1993). DO gauge AATs using SCF, MP2, and DFT APTs are referred to as SCF, semi-MP2, and semi-DFT AATS, respectively. Note that the use of the DO gauge permits the partial inclusion of correlation in AATs when correlated APTs are available.

Frequencies, dipole strengths and rotational strengths derived from harmonic force fields, APTs and AATs were used to synthesize absorption and VCD spectra using Lorentzian band shapes (Kawiecki 1988).

Calculations used 3-21G (Hehre et al. 1986), 6-31G\* (Hehre et al. 1986), and [5s4p2d/3s2p] TZ/2P (Stephens et al. 1990) basis sets.

### 3. RESULTS

We begin by comparing unpolarized absorption and VCD spectra calculated using 6-31G\* B3LYP DFT force fields to experimental spectra. The 6-31G\* basis set (Hehre et al. 1986) is widely used in ab initio computational studies of organic molecules, especially in calculations including correlation (e.g., MP2). We examine only the mid-IR spectral region and exclude the C-H stretching region from the discussion. Without explicit consideration of anharmonicity, calculations of C-H stretching spectra are futile. Experimental mid-IR VCD spectra are limited to frequencies  $\geq 650 \text{ cm}^{-1}$  (the current lower limit of existing instrumentation). We limit our discussion of unpolarized absorption spectra to the region over which VCD spectra have been measured.

Figure 2a–d shows calculated and experimental mid-IR spectra for 1. The lower frequency limit of the experimental spectra is  $690\text{ cm}^{-1}$ . Comparison of calculated and experimental absorption spectra yields the unambiguous assignment of fundamentals 7–23 shown in Figures 2a and 2b. The assignment is further detailed in Table 1. Calculated frequencies are in all cases greater than experimental frequencies; the average deviation of calculated and experimental frequencies is  $39\text{ cm}^{-1}$  (3.3%) and the maximum deviation is  $74\text{ cm}^{-1}$  (5.1%).

Calculated and experimental VCD spectra are compared in Figures 2c and 2d. VCD is observed for all fundamentals excepting 22 and 23. The agreement of calculated and observed VCD intensities is quite good, being worst for fundamentals 12 and 18. The sign is correctly predicted for all bands except 18.

Figure 3 shows calculated and experimental mid-IR spectra for 2. The lower frequency limit of the experimental spectra is  $800\text{ cm}^{-1}$ . Comparison of calculated and experimental absorption spectra yields the assignment of the fundamentals 10–38 shown in Figures 3a and 3b. The assignment is unambiguous for the fundamentals in the range  $800\text{--}1,300\text{ cm}^{-1}$ ; above  $1,300\text{ cm}^{-1}$ , the lower intensity and greater congestion of the spectrum, together with the greater probability of contributions from nonfundamentals, lessens the confidence level somewhat. The assignment is further detailed in Table 2. Calculated frequencies are in all cases greater than experimental frequencies; the average deviation of calculated and experimental frequencies is  $36\text{ cm}^{-1}$  (2.9%) and the maximum deviation is  $75\text{ cm}^{-1}$  (5.2%).

Comparison of the calculated and experimental VCD spectra is complicated by the much lower signal-to-noise ratio of the experimental VCD spectrum, in comparison to the absorption spectrum. Fundamentals 12–15, 17–20, 23, 24, 26, 28–33, and 38 exhibit clearly defined VCD. For these bands, the calculated VCD agrees in sign with the exception of 28 and 29. Below  $1,300\text{ cm}^{-1}$ , the agreement of calculated and observed VCD intensities is quite good; the agreement is worst for fundamental 26. The calculation significantly underestimates the intensities of the bands in the region  $1,300\text{--}1,400\text{ cm}^{-1}$ .

Figure 4 shows calculated and experimental mid-IR spectra for 3. The lower frequency limit of the experimental spectra is  $900\text{ cm}^{-1}$ . Comparison of calculated and experimental absorption spectra yields the assignment of the fundamentals 24–58 shown in Figures 4a and 4b. Fundamentals 29–40, 42–44, 46–50 are clearly resolved and unambiguously assignable. Fundamentals 41 and 45 are weak and not clearly resolved. The regions  $900\text{--}950\text{ cm}^{-1}$  and  $1,440\text{--}1,500\text{ cm}^{-1}$  are more congested and the assignments of fundamentals 24–28 and 51–58 are less certain. The assignment is further detailed in



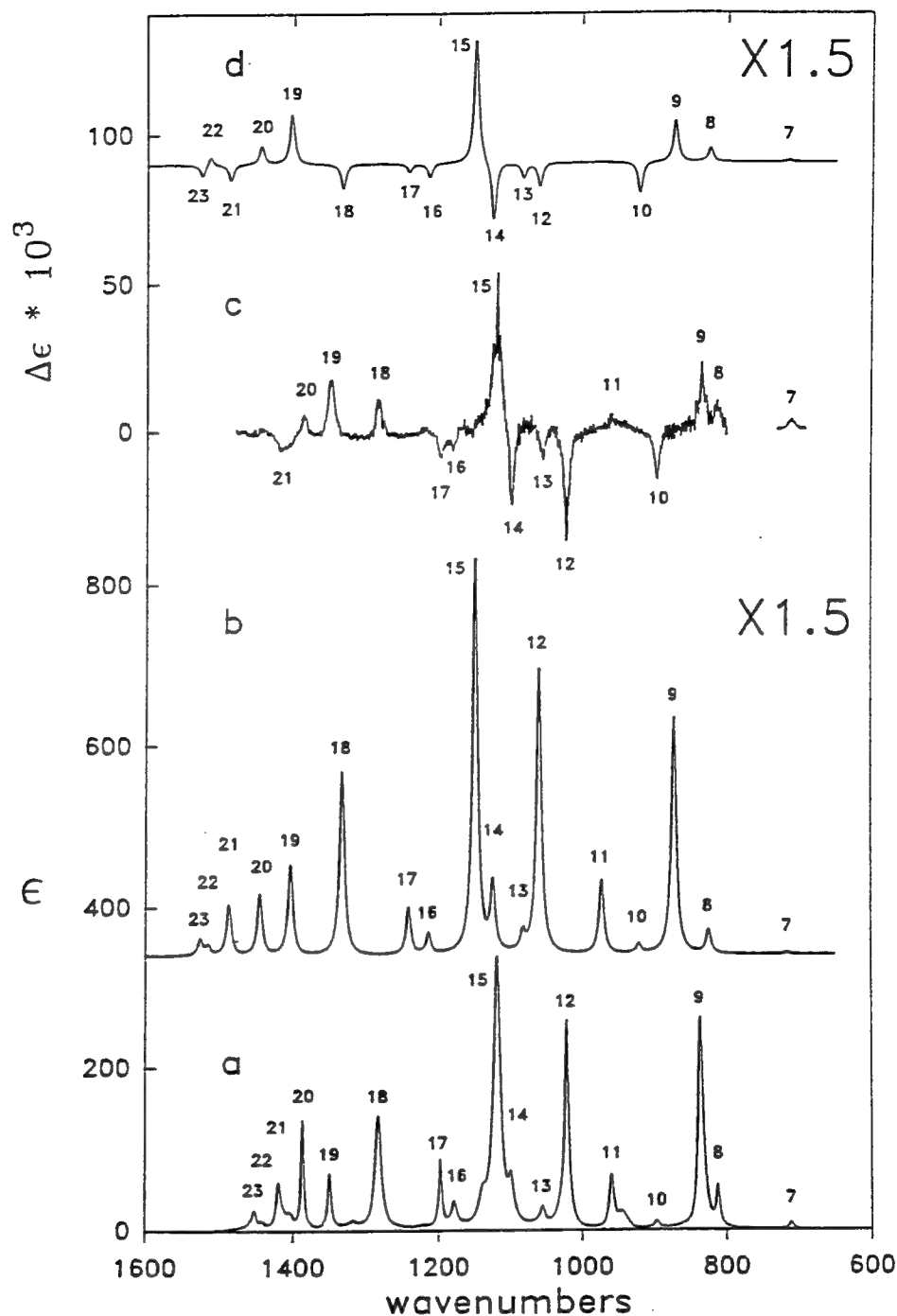


Figure 2. Mid-IR absorption and VCD spectra of R – (+) – 1. Experimental spectra (a and c) from (Devlin et al. to be published). Calculated spectra (b and d) use 6-31G\* B3LYP/DFT force field and APTs; AATs are 6-31G\* semi-B3LYP/DFT. Calculated spectra use Lorentzian band shapes with  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands. Note that some of the differences between calculated and experimental absorption and VCD intensities originate in deviations in experimental band widths from  $\gamma = 4.0 \text{ cm}^{-1}$ . The assignment of fundamentals is indicated; see also Table 1.

Table 1. 4-Methyl-2-Oxetanone<sup>a</sup>

Fundamental <sup>b</sup>	Calculation <sup>c</sup>						Experiment <sup>d</sup>		
	TZ/2P			6-31G*					
	$\bar{\nu}$	D	R	$\bar{\nu}$	D	R	$\bar{\nu}$	D	R
23	1,500	13.2	-5.3	1,526	10.1	(8.3)	1,453	25.1	-2.2
22	1,489	7.9	5.3	1,515	5.8	(3.2)	1,441	2.5	2.8
21	1,462	42.6	-11.5	1,487	32.6	(26.8)	1,419	35.1	-9.5
20	1,422	51.2	10.8	1,445	40.6	(32.7)	1,387	58.2	13.3
19	1,389	50.0	28.3	1,404	62.2	(65.9)	1,350	39.7	42.2
18	1,316	111.5	3.5	1,334	132.5	(188.0)	1,284	161.3	25.5
17	1,229	44.2	-3.7	1,242	36.1	(27.6)	1,198	47.4	-20.7
16	1,204	19.0	-5.0	1,214	16.2	(18.9)	1,178	34.6	-17.3
15	1,137	326.7	98.9	1,148	330.7	(422.8)	1,118	482.6	178.3
14	1,113	87.1	-57.9	1,124	57.0	(85.1)	1,099	51.2	-82.7
13	1,076	11.0	-5.7	1,082	15.4	(26.5)	1,055	40.4	-23.2
12	1,041	268.0	-49.8	1,060	260.1	(338.9)	1,022	251.0	-102.4
11	966	91.1	6.7	973	73.4	(77.3)	959	69.8	11.5
10	914	8.2	-27.2	921	9.8	(19.2)	896	10.2	-54.4
9	850	309.9	46.3	872	259.0	(424.1)	836	371.5	78.1
8	817	34.1	9.7	824	27.6	(31.2)	812	54.9	28.9
7	712	2.1	2.1	715	3.0	(6.1)	711	13.3	15.5

<sup>a</sup>  $\bar{\nu}$  in  $\text{cm}^{-1}$ , D in  $10^{-40} \text{esu}^2 \text{cm}^2$ , R in  $10^{-44} \text{esu}^2 \text{cm}^2$ . Rotational strengths are for the R - (+) enantiomer.<sup>b</sup> Fundamentals are numbered in order starting from the lowest frequency. Six fundamentals of **1** lie below  $700 \text{cm}^{-1}$ .<sup>c</sup> B3LYP/DFT harmonic force field and APTs, semi-B3LYP/DFT AATs. Numbers in parenthesis are for B3LYP/DFT harmonic force field; SCF APTs and AATs.<sup>d</sup> Devlin et al. (to be published.)

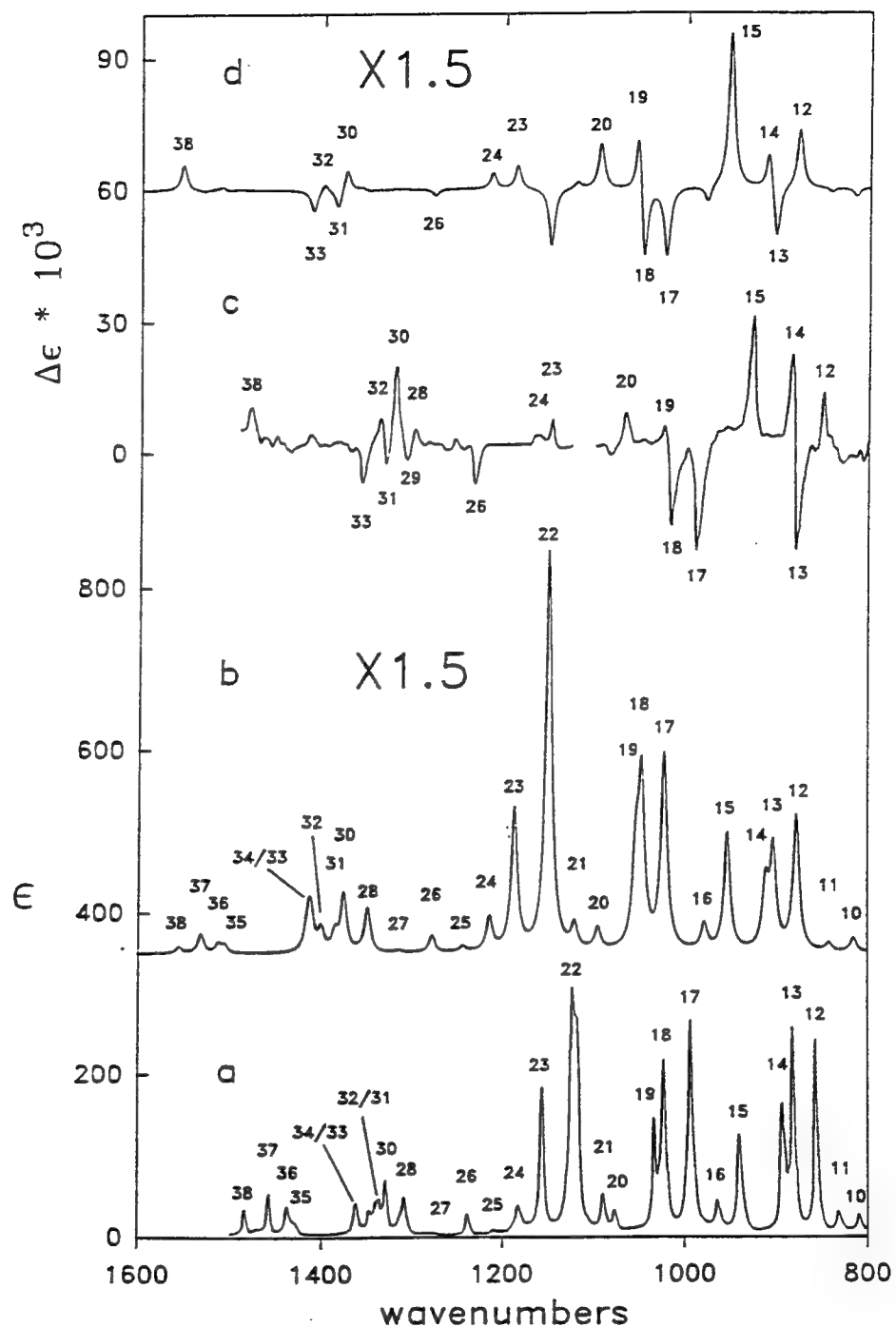


Figure 3. Mid-IR absorption and VCD spectra of (1R, 5S) - (+) - 2. Experimental spectra (a and c) from Eggimann, Shaw, and Wieser (1991) and Eggimann et al. (1993). Calculated spectra (b and d) use 6-31G\* B3LYP/DFT force field and APTs; AATs are 6-31G\* semi-B3LYP/DFT.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands. The assignment of fundamentals is indicated; see also Table 2.

Table 2. 6,8-Dioxabicyclo[3.2.1]Octane<sup>a</sup>

Fundamental <sup>b</sup>	Calculation <sup>c</sup>			Experiment <sup>d</sup>		
	$\bar{\nu}$	D	R	$\bar{\nu}$	D	R
38	1,555	4.1	7.2	1,484	13.1	19.4
37	1,532	12.0	-0.6	1,458	20.7	
36	1,513	5.4	1.0	1,438	11.9	
35	1,506	4.8	-0.4	1,435	5.8	
				1,430	6.7	
34	1,415	17.2	-0.3	1,365	11.1	
33	1,412	25.0	-6.5	1,362	14.9	-18.8
32	1,401	14.6	2.4	1,343	21.8	24.9
31	1,386	11.8	-6.3	1,338	11.4	-29.8
30	1,376	39.4	7.0	1,331	37.6	52.3
29	1,359	0.8	0.7	1,315	5.8	-15.2
28	1,349	30.9	-0.6	1,310	28.1	11.6
27	1,314	1.7	0.2	1,276	0.8	
26	1,278	12.8	-2.2	1,240	11.5	-16.4
25	1,243	4.2	0.2	1,211		
24	1,214	25.9	5.7	1,182	34.4	
23	1,187	112.6	8.6	1,157	126.3	13.6
22	1,149	328.7	-21.7	1,124	171.5	
				1,119	205.9	
21	1,120	20.4	2.5	1,089	33.4	-9.6
20	1,095	18.6	18.0	1,076	17.0	19.3
19	1,053	78.0	30.0	1,033	77.4	20.3
18	1,047	149.9	-36.0	1,022	190.8	-62.3
17	1,023	180.7	-29.0	993	248.5	-80.0
16	979	25.0	-7.3	962	32.6	6.4
15	953	117.3	71.5	939	120.2	88.0
14	911	64.5	20.5	893	120.1	63.3
13	903	103.2	-27.9	882	216.0	-74.0
12	878	145.3	29.4	857	174.6	32.5
11	842	8.9	-2.3	832	26.1	
10	815	16.7	-4.5	809	21.2	

<sup>a</sup>  $\bar{\nu}$  in  $\text{cm}^{-1}$ , D in  $10^{-40} \text{esu}^2 \text{cm}^2$ , R in  $10^{-44} \text{esu}^2 \text{cm}^2$ . Rotational strengths are for the (1R, 5S) - (+) enantiomer.

<sup>b</sup> Fundamentals are numbered in order starting from the lowest frequency. Nine fundamentals of 2 lie below  $800 \text{cm}^{-1}$ .

<sup>c</sup> 6-31G\* B3LYP/DFT harmonic force field and APTs; 6-31G\* semi-B3LYP/DFT AATs.

<sup>d</sup> Eggimann, Shaw, and Wieser (1991) and Eggimann et al. (1993). Note that our assignment of fundamentals differs from that of Wieser and coworkers. Where our assignments are not unambiguous, all alternative possibilities are indicated.



Table 3. Calculated frequencies are in all cases greater than experimental frequencies. The average deviation of calculated and experimental frequencies is  $41\text{ cm}^{-1}$  (3.2%); the maximum deviation is  $79\text{ cm}^{-1}$  (5.3%).

Comparison of the calculated and experimental VCD spectra shown in Figures 4c and 4d is again complicated by the lower signal-to-noise ratio of the experimental VCD spectrum. Fundamentals 24, 25, 27, 30–32, 36, 37, 39, 42, 44, 46–50, and 57 exhibit clearly defined VCD. For these bands, the calculated VCD agrees in sign in every case with the exception of fundamental 30. The agreement of calculated and observed VCD intensities is quite good, being worst for fundamentals 32, 44, and 50. Despite the greater complexity of the regions  $900\text{--}950\text{ cm}^{-1}$  and  $1,440\text{--}1,500\text{ cm}^{-1}$ , calculated and experimental VCD spectra are in quite good agreement.

The level of agreement of calculated and experimental mid-IR absorption and VCD spectra exhibited in Figures 2–4 is impressive. However, the agreement is not perfect. The possible sources of error are: (1) errors in the force field, APTs, and AATs due to the incompleteness of the 6-31G\* basis set; (2) errors in the local AATs due to the absence of correlation; (3) errors in the force field and APTs due to the inexactness of the B3LYP density functional; and (4) the absence of an harmonicity and condensed phase/solvent perturbations in the calculational formalism.

Basis set error can be determined from calculations using large basis sets. In the case of 1, we have carried out calculations using a [5s4p2d/3s2p], TZ/2P, basis set, with the results given in Figure 5 and Table 1. The agreement of calculated and experimental frequencies is improved: the average and maximum deviations are now  $25\text{ cm}^{-1}$  (2.0%) and  $48\text{ cm}^{-1}$  (3.3%), respectively. Both calculated absorption and VCD intensities are in better agreement with experiment. The improvement is more marked in the case of the VCD spectrum: fundamental 18 is now correct in sign and the intensities of fundamentals 11 and 12 are in significantly improved agreement with experiment. The greater basis set dependence of the calculated VCD spectra than of the calculated absorption spectra is attributable to the greater basis set error in the local AATs than in the force field and APTs. This is verified by calculations using the 6-31G\* force field and APTs together with TZ/2P local AATs, the results of which are also given in Figure 5.

We are not yet able to examine the magnitudes of errors originating in the absence of correlation in local AATs by carrying out calculations in which correlation is included. However, we can examine the

Table 3. Camphor<sup>a</sup>

Fundamental <sup>b</sup>	Calculation <sup>c</sup>				Experiment <sup>d</sup>	
	$\bar{\nu}$	D	R	g	$\bar{\nu}$	g
58	1,560	10.7	-1.6	-0.6	1,481	
57	1,547	11.4	8.4	2.9	1,470	2.1
56	1,542	0.8	1.4	7.0		
55	1,531	9.1	0.3	0.1		
54	1,526	6.7	4.1	2.4		
53	1,521	12.0	3.3	1.1	1,453	
52	1,516	12.9	-0.4	-0.1	1,449	
51	1,513	6.6	-0.1	-0.1		
50	1,489	24.8	-1.0	-0.2	1,417	-0.6
49	1,455	18.9	-4.5	-1.0	1,391	-0.9
48	1,438	11.7	1.9	0.6	1,377	
47	1,434	12.4	-0.8	-0.3	1,371	
46	1,361	14.2	6.9	1.9	1,323	1.7
45	1,347	2.5	-1.5	-2.4	1,299	
44	1,340	6.6	-2.2	-1.3	1,295	
43	1,312	21.6	-2.9	-0.5	1,277	0.5
42	1,284	10.1	11.0	4.4	1,245	8.9
41	1,279	0.1	1.0	40.0		
40	1,258	10.5	3.9	1.5	1,220	
39	1,235	17.5	-8.8	-2.0	1,198	
38	1,226	2.7	1.1	1.6	1,192	
37	1,197	12.5	10.3	3.3	1,166	5.6
36	1,181	2.0	-5.1	-10.2	1,154	-5.8
35	1,155	3.9	6.6	6.8	1,128	3.1
34	1,128	17.6	-7.0	-1.6	1,094	-0.6
33	1,108	5.5	-9.4	-6.8	1,079	
32	1,064	76.8	-11.2	-0.6	1,045	-2.5
31	1,045	97.3	-0.9	0.0	1,021	-1.3
30	1,040	7.9	-4.8	-2.4	1,012	2.2
29	1,009	0.3	-0.7	-9.3	986	-4.6
28	970	10.9	2.9	1.1	950	
27	966	4.6	-11.4	-9.9		
26	951	1.7	1.1	2.6	936	
25	950	12.9	18.6	5.8	925	10.7
24	927	5.7	-9.7	-6.8	913	-12.5

<sup>a</sup>  $\bar{\nu}$  in  $\text{cm}^{-1}$ , D in  $10^{-40} \text{esu}^2 \text{cm}^2$ , R in  $10^{-44} \text{esu}^2 \text{cm}^2$ ; anisotropy ratio g in  $10^{-4}$ . Rotational strengths are for the (1R, 4R) - (+) enantiomer.

<sup>b</sup> Fundamentals are numbered in order starting from the lowest frequency. Twenty-three fundamentals of **3** lie below  $900 \text{cm}^{-1}$ .

<sup>c</sup> 6-31G\* B3LYP/DFT harmonic force field and APTs; 6-31G\* semi-B3LYP/DFT AATs.

<sup>d</sup> Devlin and Stephens (1994) and Nafie (1984).

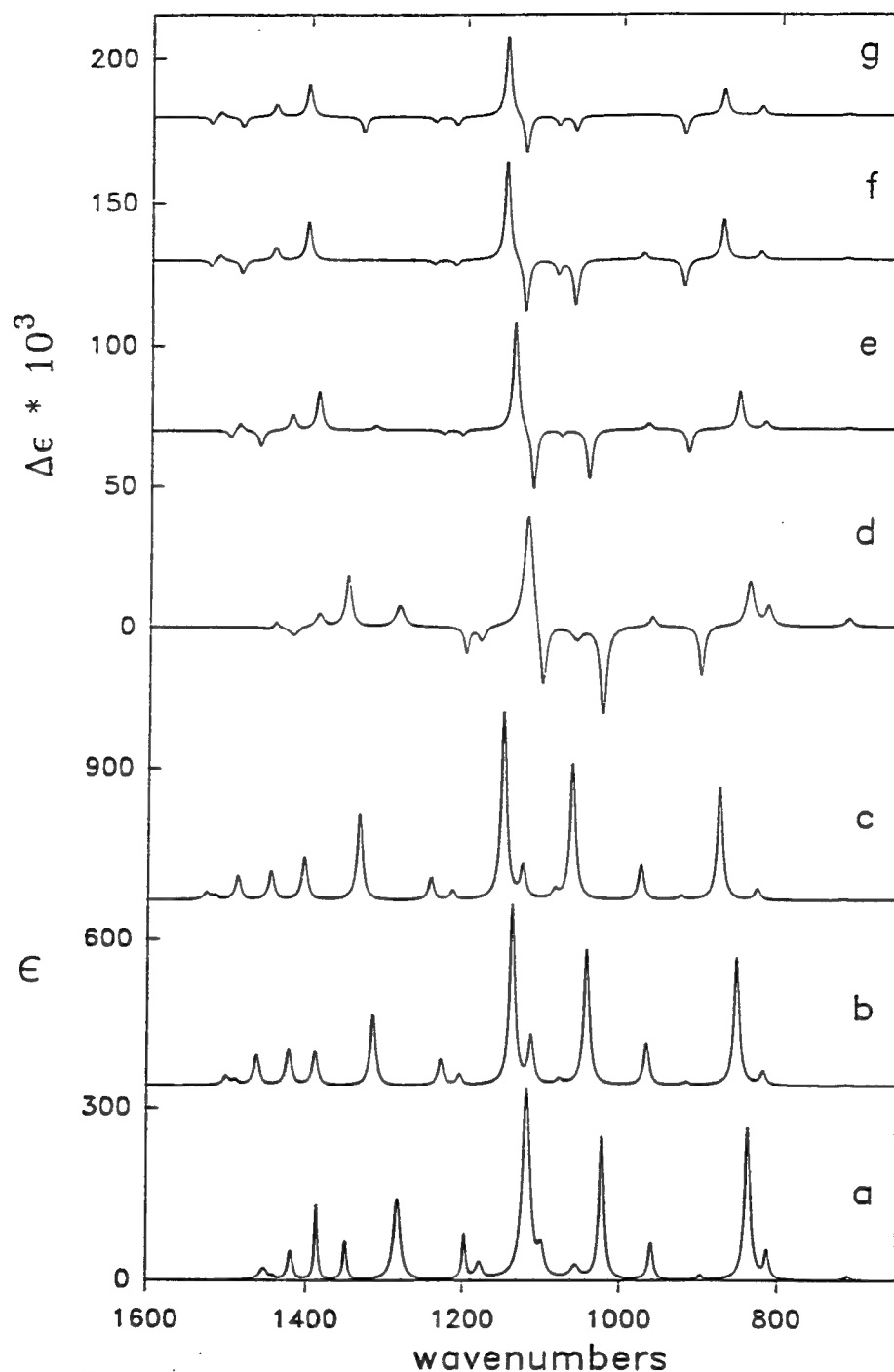


Figure 5. Mid-IR absorption and VCD spectra of R – (+) – 1. Spectra a and d are obtained by Lorentzian fitting of the experimental spectra (Figures 2a and 2c) followed by elimination of all nonfundamental bands. Calculated spectra (b, c, e, f, and g) use B3LYP/DFT force field and APTs; AATs are semi-B3LYP/DFT. In b and e, the basis set is TZ/2P; in c and g it is 6-31G\*. In f, the force field and APTs are 6-31G\* while the local AATs are TZ/2P.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands in all calculated spectra.



results of calculations in which correlation is not included in the APTs. It is not unreasonable to expect that the inclusion of correlation in APTs and in AATs will give rise to contributions to rotational strengths of comparable order of magnitude. The results for 1 obtained using 6-31G\* SCF APTs in place of 6-31G\* B3LYP/DFT APTs are given in Figure 6 and Table 1. Both absorption and VCD spectra are qualitatively unaffected. Quantitatively, the changes are larger in the absorption intensities, which are generally increased by the substitution of SCF for B3LYP/DFT APTs. It is reasonable to conclude that inclusion of correlation in the calculation of local AATs will not cause major qualitative changes in the calculated VCD spectrum.

At this time, there does not appear to be any density functional available whose accuracy is significantly greater than that of the B3LYP functional. We cannot therefore directly examine the errors in B3LYP/DFT calculations by comparison to more accurate calculations. However, we can examine the sensitivity of the calculated spectra to alternative, less accurate choices of density functional. The results for 1 obtained using two widely employed functionals—LSDA and BLYP—are compared to those obtained using B3LYP in Figure 7. Both functionals give absorption and VCD spectra substantially different from and in much worse agreement with experiment than given by the B3LYP functional. It is clear that the LSDA and BLYP harmonic force fields are significantly less reliable than the B3LYP force field. In turn, it is certainly possible that some of the errors in predicted B3LYP absorption and VCD spectra are attributable to residual inexactitude in the B3LYP functional.

The results shown in Figure 5 and Table 1 demonstrate that the 6-31G\* B3LYP force field is not substantially improved if a much larger basis set is substituted for 6-31G\*. It is therefore of interest to examine the consequences of using a smaller basis set. Spectra calculated for 1 using the 3-21G basis set are shown in Figure 8. Both absorption and VCD spectra are substantially different from those obtained at the 6-31G\* basis set level and in much worse agreement with experiment. It is clear that a basis set at least as large as 6-31G\* is mandatory if useful agreement with experiment is to be obtained.

Finally, in Figure 9, we compare the spectra for 1 calculated using the 6-31G\* B3LYP/DFT force field to the spectra obtained using 6-31G\* SCF and 6-31G\* MP2 force fields. APTs are calculated at the same level as the force field; local AATs are in all cases calculated at the 6-31G\* SCF level. The MP2 methodology yields spectra quite similar to those obtained using DFT with the B3LYP functional and in slightly worse agreement with experiment. The most noticeable difference is in the relative absorption intensities of fundamentals 14 and 15. In contrast, the SCF methodology yields quite different spectra in

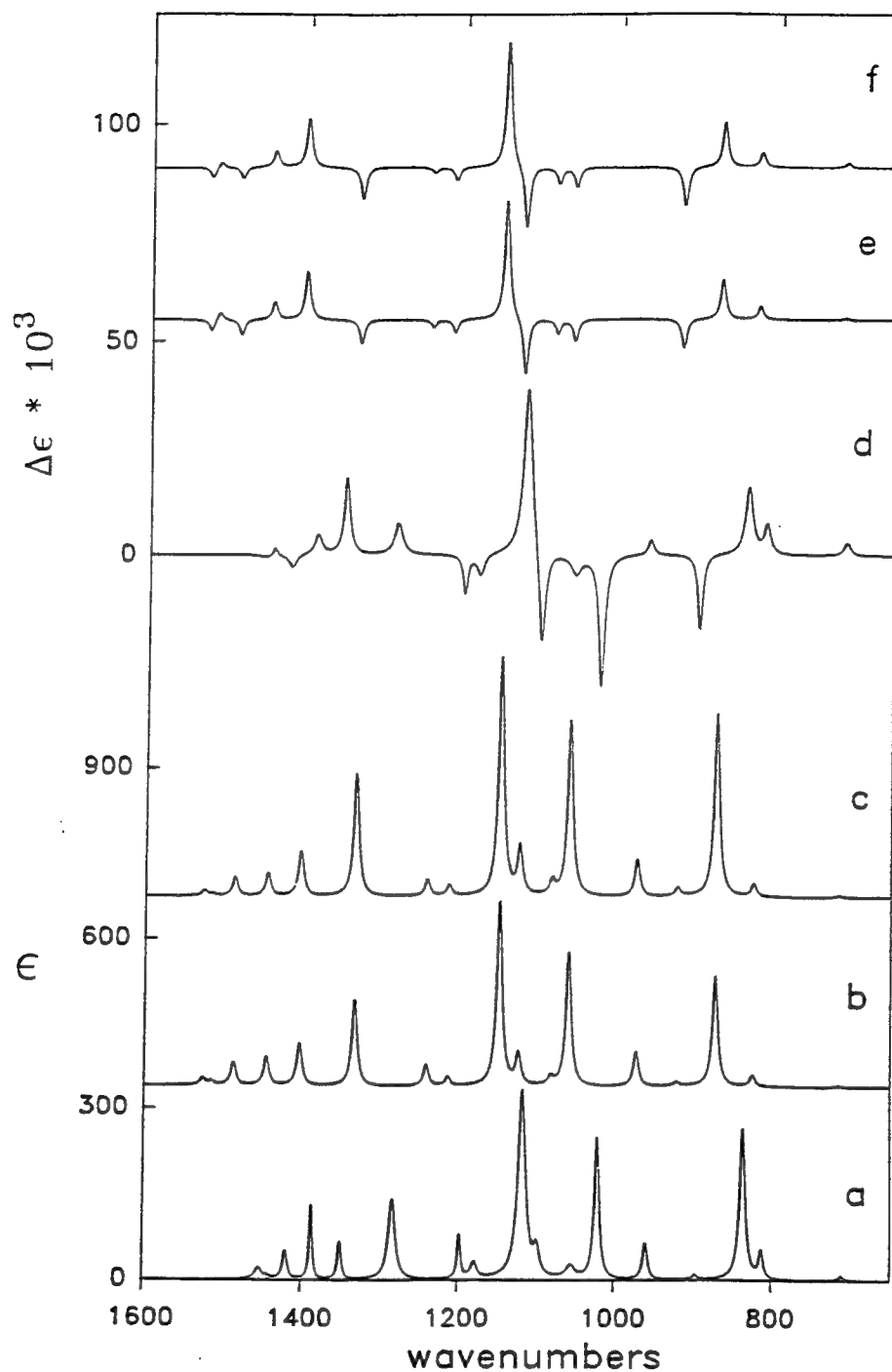


Figure 6. Mid-IR absorption and VCD spectra of R – (+) – 1. Spectra a and d are the fundamental experimental spectra from Figures 5a and 5d. Calculated spectra (b, c, e, and f) use the 6-31G\* B3LYP/DFT force field. In b and e, the APTs are 6-31G\* B3LYP/DFT and the AATs are 6-31G\* semi-B3LYP/DFT. In c and f, the APTs and AATs are 6-31G\* SCF.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands in all calculated spectra.

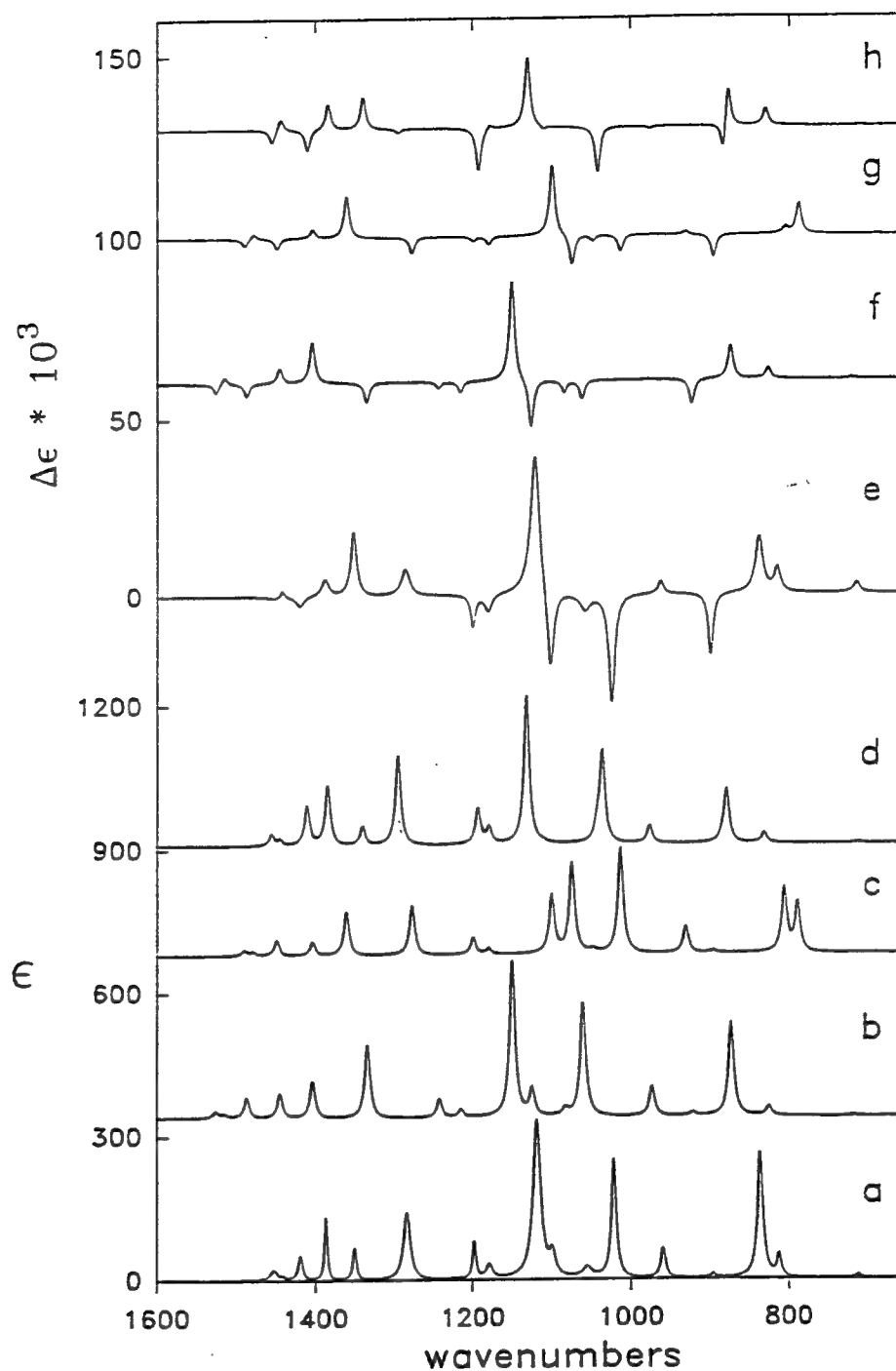


Figure 7. Mid-IR absorption and VCD spectra of R - (+) - 1. Spectra a and e are the fundamental experimental spectra from Figures 5a and 5d. Calculated spectra (b, c, d, f, g, and h) use 6-31G\* DFT force fields and APTs; AATs are 6-31G\* semi-DFT. In b and f, the density functional is B3LYP; in c and g, it is BLYP; in d and h, it is LSDA.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands in all calculated spectra.

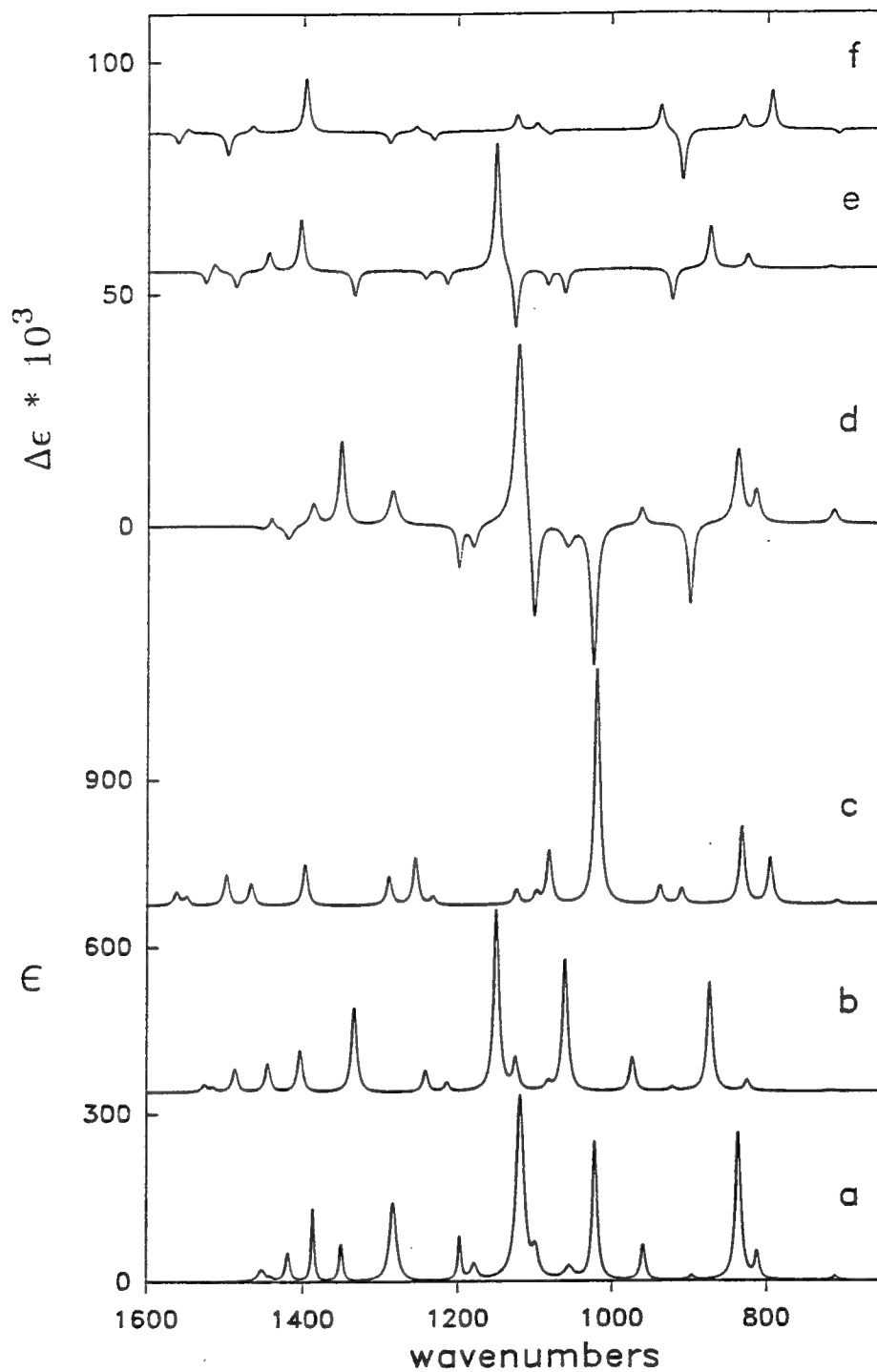


Figure 8. Mid-IR absorption and VCD spectra of R – (+) – 1. Spectra a and d are the fundamental experimental spectra from Figures 5a and 5d. Calculated spectra (b, c, e, and f) use B3LYP/DFT force field and APTs; AATs are semi-B3LYP/DFT. In b and e, the basis set is 6-31G\*; in c and f, it is 3-21G.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands in all calculated spectra.

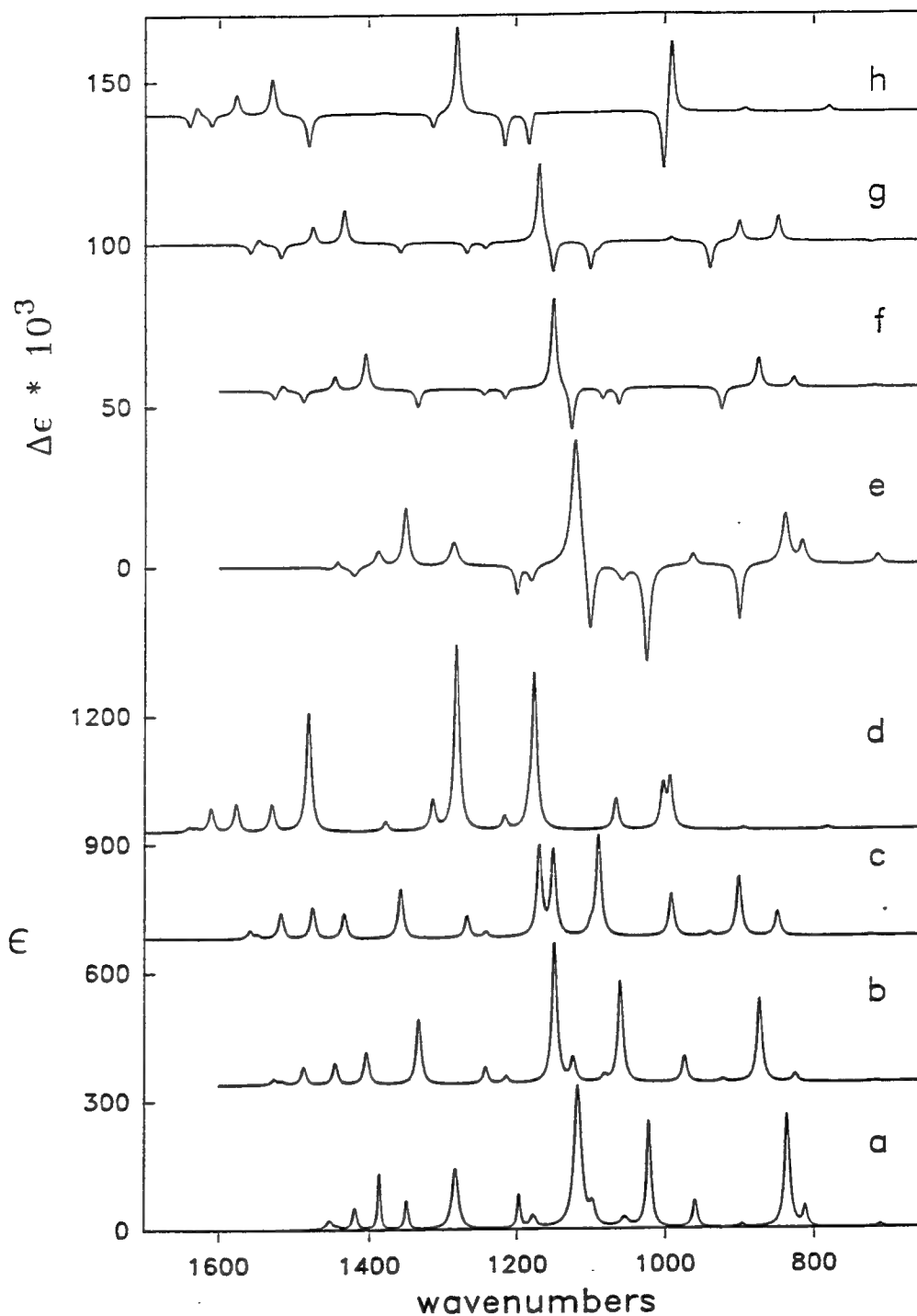


Figure 9. Mid-IR absorption and VCD spectra of R - (+) - 1. Spectra a and e are the fundamental experimental spectra from Figures 5a and 5d. Calculated spectra b and f use 6-31G\* B3LYP/DFT force field and APTs; AATs are semi-B3LYP/DFT. In c and g, the force field and APTs are 6-31G\* MP2; AATs are semi-MP2. In d and h, the force field, APTs, and AATs are 6-31G\* SCF.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands in all calculated spectra.

very much worse agreement with experiment. The importance of including correlation in the calculation of harmonic force fields is forcefully demonstrated by these results. At the same time, the B3LYP/DFT method is clearly shown to be highly competitive with the MP2 methodology in including correlation.

Analogous calculations for 2 and 3 to those for 1 presented in Figures 6–9 confirm the generality of the conclusions arrived at above in the case of 1. These calculations will be reported elsewhere. (Note that 6-31G\* MP2 calculations have already been published for 3 [Devlin and Stephens 1994]).

In the case of 2, a second conformation is possible in which the six-membered ring is in a boat, rather than a chair, conformation. Ab initio calculations (6-31G\* SCF, MP2, and B3LYP/DFT) predict a 4–6 kcal/mole energy difference. Mid-IR absorption and VCD spectra predicted for the "boat" configuration of 2 are compared to the experimental spectra in Figure 10. In contrast to the spectra predicted for the "chair" conformation, the agreement with the experimental spectra is very poor. The difference is especially dramatic in the case of the VCD spectra. As expected, the "chair" conformation of 2 is unquestionably that existing experimentally.

#### 4. DISCUSSION

We have demonstrated that calculations of the mid-IR absorption and VCD spectra of 1–3 based on 6-31G\* B3LYP/DFT harmonic force fields are (1) in impressive agreement with experiment; (2) substantially more accurate than calculations using the LSDA and BLYP density functionals; (3) comparable in accuracy to calculations based on 6-31G\* MP2 force fields, while much less computationally demanding. Substitution of TZ/2P and 3-21G basis sets for 6-31G\* leads to spectra of very similar and much worse accuracy, respectively.

While the considerable accuracy of DFT calculations using "modern" density functionals has been widely reported (Ziegler 1991; Labanowski and Andzelm 1991; Andzelm and Wimmer 1992; Johnson, Gill, and Pople 1993; Handy, Murray, and Amos 1993), the sensitivity of predicted vibrational spectra to the choice of density functional was not clear prior to this work. Comparisons of harmonic frequencies calculated using various functionals, including LSDA ( $\equiv$ SVWN) and BLYP, to experimental harmonic frequencies did not suggest large differences in accuracy (Johnson, Gill, and Pople 1993). However, dipole and rotational strengths depend on vibrational coordinates, which are much more sensitive to the accuracy of the force field than are vibrational frequencies. It is therefore not surprising to find that

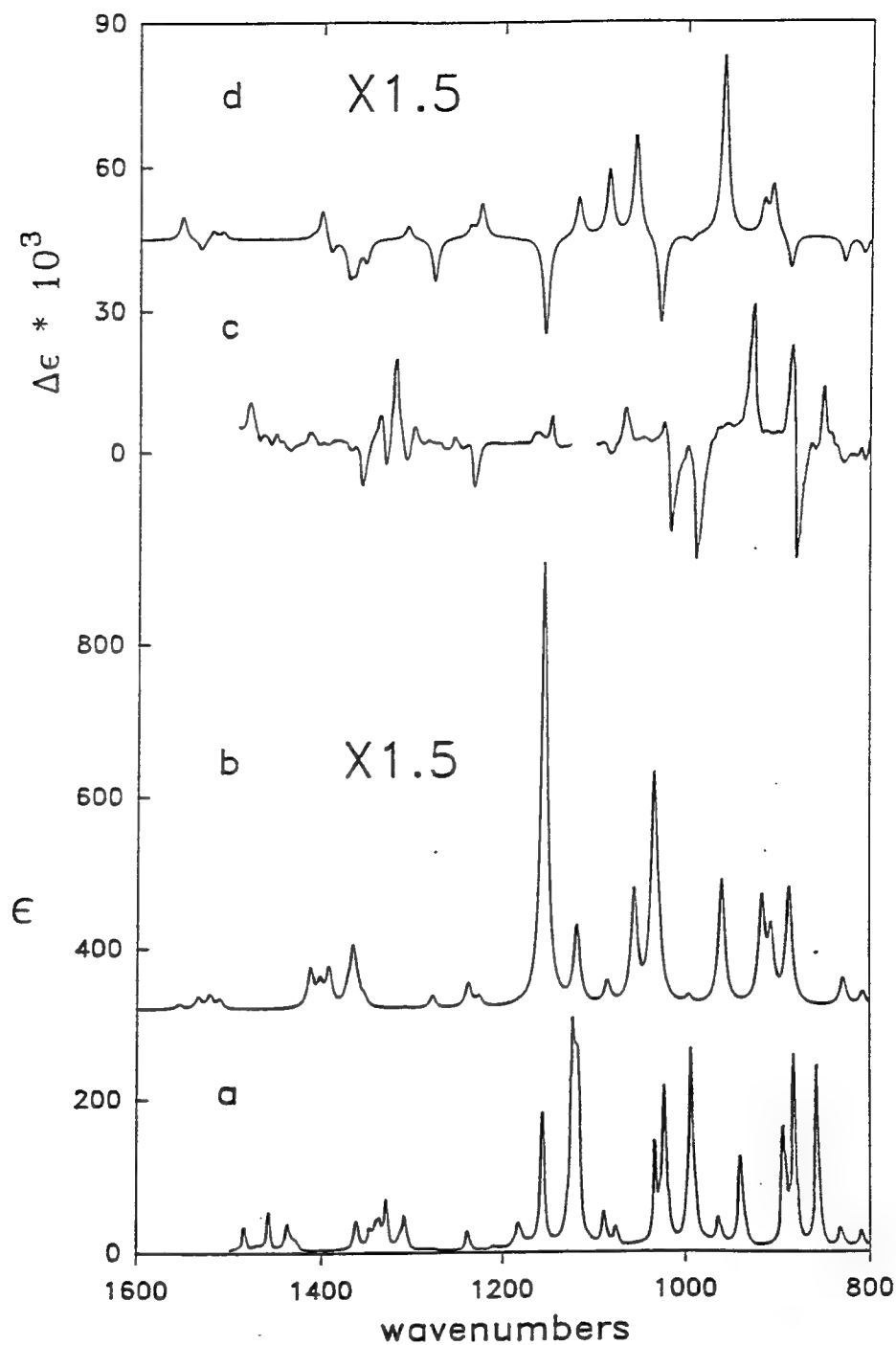


Figure 10. Mid-IR absorption and VCD spectra of (1R, 5S) - (+) - 2. Experimental spectra (a and c) are as in Figures 3a and 3c. Calculated spectra b and d are for the boat conformation of 2 and use 6-31G\* B3LYP/DFT force field and APTs; AATs are 6-31G\* semi-B3LYP/DFT.  $\gamma = 4.0 \text{ cm}^{-1}$  for all bands.

calculated spectra are, in fact, quite sensitive to the choice of density functional. The really new result is that the hybrid, B3LYP, functional gives spectra of impressive accuracy while the LSDA and BLYP functionals do not. Our work thus defines a threshold level of accuracy for density functionals in future calculations of mid-IR vibrational spectra. At the same time, it is clear that further improvements in density functionals may well lead to significantly improved vibrational spectra. B3LYP could be replaced as the functional of choice in the near future!

Our work also further illuminates the relative accuracies of DFT and MP2 harmonic force fields. At the B3LYP level, DFT and MP2 force fields are very similar in accuracy when this is gauged by the comparison of calculated and experimental mid-IR spectra for 1-3. The LSDA and BLYP DFT force fields are clearly inferior to MP2 force fields. This latter finding is surprising: it has been reported that such functionals yield harmonic frequencies comparable in accuracy with MP2 calculations (Johnson, Gill, and Pople 1993). It is possible that this difference reflects the focus of our work on mid-IR spectra, to the exclusion of hydrogenic stretching and low-frequency spectral regions, while comparisons of calculated and experimental frequencies for small molecules (the only ones for which harmonic frequencies are known) include all frequencies and are heavily weighted by hydrogenic stretching frequencies.

The conclusions we have arrived at have made use of both absorption and VCD spectra in comparing theory and experiment. While the same conclusions would have been reached if absorption or VCD spectra had been used alone, the combined use of both spectra significantly enhances the reliability of the assignments of fundamentals and of the evaluation of the relative accuracies of different calculations. The usefulness of VCD spectra for this purpose is of course dependent on the reliability with which VCD intensities can be predicted. This is lower than the reliability of predicted absorption intensities since (1) absorption intensities require only APTs, while VCD intensities require both APTs and AATs, and (2) AATs are less accurately calculated due to (a) the absence of correlation in the calculation of local AATs and (b) the greater basis set error in local AATs than in APTs. As expected, the agreement of calculated and experimental VCD spectra is generally less perfect than in the case of absorption spectra. Nevertheless, it is clear that the 6-31G\* semi-B3LYP/DFT AATs used in this work are of sufficient reliability to successfully predict the qualitative pattern of VCD intensities with a very small number of exceptions, and to support the interrogation of alternative force fields in a meaningful way.

Currently, the practical limits in calculations of harmonic force fields are imposed by the disk storage requirements. Analytical derivative calculations at the MP2 level require much more disk space than do



SCF calculations. DFT calculations have identical requirements to SCF calculations. SCF and DFT calculations can therefore be carried out for much larger molecules than are accessible to MP2 calculations. Currently, with the machines available to us (which include a CRAY C90) MP2 6-31G\* calculations on 3 are close to the limit of practicability. In contrast, DFT 6-31G\* calculations will be straightforward for molecules much larger than 3. Our results here lead to the conclusion that these calculations will be of useful accuracy as long as the B3LYP (or better) density functional is used.

## 5. CONCLUSION

The implications for the utilization of VCD spectroscopy are obvious and dramatic. The reliable prediction of VCD spectra will be routine for molecules much larger than 3. In turn, the elucidation of molecular stereochemistry from VCD spectra will be straightforward. All that remains is to choose interesting and important problems to study.

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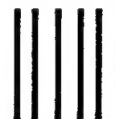
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